

# Thermodynamic properties of Pb determined from pressure-dependent critical-field measurements

N. Suresh<sup>1</sup> and J.L. Tallon<sup>1,2</sup>

<sup>1</sup>*MacDiarmid Institute for Advanced Materials and Nanotechnology,  
Industrial Research Ltd., P.O. Box 31310, Lower Hutt, New Zealand. and*

<sup>2</sup>*Victoria University, P.O. Box 600, Wellington, New Zealand*

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We have carried out extensive low-temperature (1.5 to 10 K) measurements of the critical field,  $H_c$ , for the element Pb up to a pressure of  $P = 1.2$  GPa. From this data the electronic entropy, specific heat, thermal expansion coefficient and compressibility is calculated as a function of temperature, pressure and magnetic field. The zero-field data is consistent with direct thermodynamic measurements and the  $P$ -dependence of  $T_c$  and specific heat coefficient,  $\gamma(T, P)$  allows the determination of the  $P$ -dependence of the pairing interaction.

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The thermodynamic and superconducting properties of the metal Pb have been extensively studied, including specific heat<sup>1,2</sup>, isotope effect<sup>3,4</sup>, critical field<sup>5</sup> and thermal expansion<sup>6</sup>. In addition the effects of pressure on its superconducting properties have also been well studied<sup>7,8,9</sup>. Subsequently, the use of the pressure-dependent superconducting transition temperature  $T_c(P)$  for Pb as a low-temperature manometer has also been proposed<sup>10,11,12</sup>. The above quoted references are only the early ones and one would assume that the thermodynamic properties of this material have been comprehensively investigated.

In the course of investigations into the pressure dependence of the oxygen isotope effect on  $T_c$  for the high- $T_c$  superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_8$  we used the metal Pb as an internal pressure calibrant. Using a clamp cell in a SQUID magnetometer we tracked the pressure using the reported pressure dependence of  $T_c$  for Pb<sup>10</sup>. Despite the many above-noted early studies on Pb we discovered that the pressure,  $P$ , and temperature dependence of the critical field,  $H_c$ , for Pb has not been reported except at very low pressures ( $\leq 0.03$  GPa)<sup>7</sup>. We therefore carried out a study of  $H_c(T, P)$  from 1.5 to 10 K and up to 1.2 GPa from which we have derived a full set of thermodynamic parameters. This paper presents a summary of these measurements and the deduced values of the  $T$ - and  $P$ -dependence of the electronic entropy,  $S(T, P)$ , electronic specific heat coefficient,  $\gamma(T, P)$ , thermal expansion coefficient,  $\alpha(T, P)$  and electronic compressibility,  $\kappa(T, P)$ .

The sample used was a bar of dimensions  $1.1 \times 0.93 \text{ mm}$  cross section and 5.58 mm long, shaped from Pu-ratronic 99.9985%, 2 mm diameter Pb wire from Johnson Matthey. Using the formulae of Osborn the demagnetization factor was calculated as 0.97 and this value was used throughout. The Pb sample was annealed in vacuum at 300 C for 8 hours to reduce magnetic hysteresis<sup>5</sup>. This was loaded in a 2.67 mm diameter 9 mm long Teflon capsule along with Fluorinert FC70 and FC77 mixed in 1:1 ratio as a cryogenic hydrostatic pressure medium. The sample capsule was then placed in a miniature home-built non-magnetic Be-Cu(Mico Metal 97.75% Cu, 2%

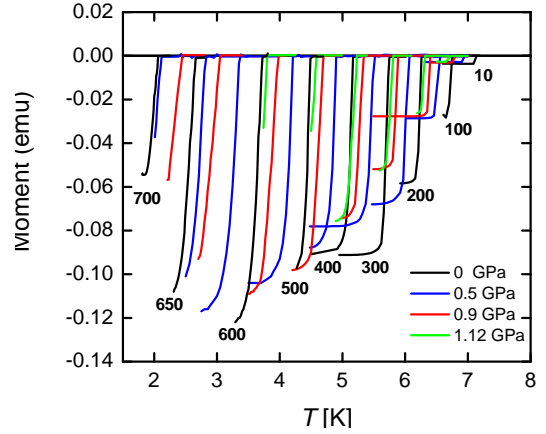


FIG. 1: (Color) Magnetization curves for the Pb sample plotted for various applied fields (annotated in Gauss as 10, 100, 200 etc) and four different pressures (0, 0.5, 0.9 and 1.15 GPa).

Be) piston clamp cell (8.8mm diameter, 65mm length, with cobalt-free tungsten-carbide pistons (Boride). The pistons of this cell are lightly tapered using electric-discharge machining<sup>13</sup>. To apply pressure the cell was preloaded before clamping at room temperature using a laboratory press with calibrated digital pressure gauge (Ashcroft Model 2089, 0.05% accuracy). The magnetization measurements were carried out in a Quantum Design MPMS SQUID magnetometer. The pressure in the sample was measured from the reported shift in  $T_c$  of Pb at zero field<sup>10</sup>. For in-field measurements the cell was always zero-field cooled to avoid hysteresis error.

Fig. 1 shows the measured  $T$ -dependence of the magnetic moment,  $M$ , up to a field of 700 G and at pressures of 0 GPa (1 bar), 0.5, 0.9 and 1.15 GPa.  $T_c$  was determined by the extrapolation to zero of the steepest slope of  $M(T)$ . This gives  $T_c(H)$  which is re-plotted in Fig. 2 as  $H_c(T, P)$  versus  $T$ . The data shows a progressive decline in both  $T_c$  and  $H_c(T)$  with increasing pressure. We will see that the combination of these two pressure effects allows access to the pressure dependence of the

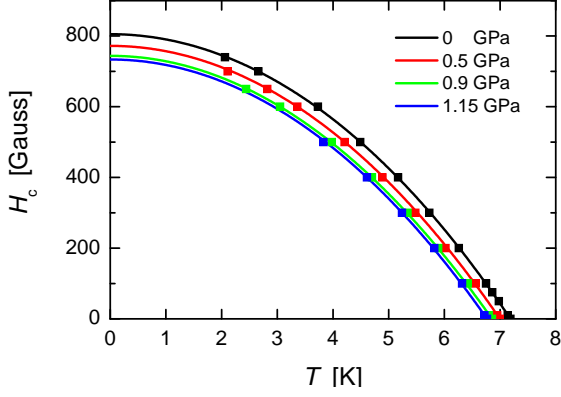


FIG. 2: (Color) The  $T$ -dependence of the critical field,  $H_c$  for pressures of 0, 0.5, 0.9 and 1.15 GPa. Data points are measured data from Fig. 1, curves are fits using eq. 2.

density of states,  $N(E_F)$ , at the Fermi level,  $E_F$  and of the pairing interaction.

To fit this data we expand  $H_c(T)$  as a power series in  $T$ . The first-order term must be zero otherwise  $S_s \neq 0$  at  $T = 0$  and the third-order term must also be zero to avoid a negative  $\gamma$  at low  $T$ . It is usual, therefore, to adopt an even polynomial of the form<sup>5</sup>

$$H_c(T, P) = H_{c0}(P) + H_{c1}(P) \times T^2 + H_{c2}(P) \times T^4 \quad (1)$$

where, as indicated, the coefficients are each an independent function of pressure. As we will see,  $H_c$  cannot be linear in  $T$  because of the third law requirement that the entropy,  $S \rightarrow 0$  as  $T \rightarrow 0$ . It turns out that the coefficients are not independent and it is common to adopt the “similitude principle” which separates the  $P$ - and  $T$ -dependent terms as follows<sup>7</sup>

$$\begin{aligned} H_c(T, P) &= H_{c0}(P) \times f(t) \\ &= H_{c0}(P) \times \{1 - \alpha \times t^2 + (1 - \alpha) \times t^4\} \end{aligned} \quad (2)$$

where  $t = T/T_c$ . A free fit of eq. (1) to the data consistently yielded  $H_{c2}/H_{c0}$  very close in value to  $1 - H_{c1}/H_{c0}$ , consistent with eq. (2). We therefore proceeded to fit the data with eq. (2) for all subsequent analysis. The fits are shown by the solid curves through the data shown in Fig. 2. We obtain  $H_{c0}$  values of 804.08, 770.88, 739.99 and 729.01 Gauss for  $P = 0, 0.5, 0.9$  and 1.15 GPa, respectively. A linear fit yields

$$H_{c0}(P) = (803.72 - 67.028P) \text{ Gauss} \quad (3)$$

This now allows the scaling of all the data by plotting  $H_c(T, P)/H_{c0}(P)$  versus  $t^2$  as shown in Fig. 3. The small departure from linearity in Fig. 3 reflects the small quartic term ( $\alpha = 0.95475$ ;  $1 - \alpha = 0.04525$ ) and the scaled data in Fig. 3 allows a global fit to determine  $\alpha$  that provides an overall consistency in the data fits that is necessary when second derivatives of  $H_c(T, P)$  are used to determine the electronic specific heat coefficient, thermal expansion coefficient or compressibility.

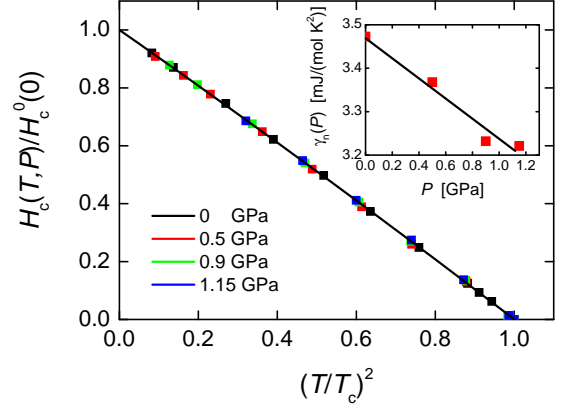


FIG. 3: (Color) Scaling of the  $T$ -dependent critical field, showing  $H_c(T, P)/H_c(T = 0, P)$  versus  $t^2 = (T/T_c)^2$  for pressures of 0, 0.5, 0.9 and 1.15 GPa. The solid curve is the function  $f(T) = 1 - 0.95475t^2 - 0.04525t^4$ . Inset:  $\gamma_n$  calculated from eqn. (6).

These parameters may be determined as follows. We restrict our thermodynamic parameters to the electronic contribution, thus ignoring the lattice contribution to the specific heat or thermal expansion. The difference in free energy between the normal and superconducting states at the same  $T$  and  $P$  is given by

$$G_s(T, P) = G_n(T, P) - \frac{1}{2} \mu_o H_c(T, P)^2 \times V_M \quad (4)$$

where  $\mu_o$  is the permeability of free space and  $V_M$  is the molar volume. As shown by Shoenberg<sup>14</sup> the thermodynamic parameters are obtained by differentiation with respect to  $T$  and  $P$ , giving

$$\begin{aligned} S_s(T, P) &= S_n(T, P) + \mu_o H_c V_M (\partial H_c / \partial T)_P \\ \gamma_s &= \gamma_n + \mu_o V_M (\partial H_c / \partial T)_P^2 \\ &\quad - \mu_o H_c V_M (\partial^2 H_c / \partial T^2)_P \\ V_s &= V_n - \mu_o H_c V_M (\partial H_c / \partial P)_T \\ \alpha_s &= \alpha_n - \mu_o (\partial H_c / \partial T)_P \times (\partial H_c / \partial P)_T \\ &\quad - \mu_o H_c (\partial^2 H_c / \partial T \partial P) \\ \kappa_s &= \kappa_n + \mu_o (\partial H_c / \partial P)_T^2 \\ &\quad + \mu_o H_c (\partial^2 H_c / \partial P^2)_T \end{aligned} \quad (5)$$

Here terms such as  $(1/2) \mu_o H_c^2 V_M \alpha_{tot}$  in the entropy or  $\mu_o \kappa_{tot} H_c (\partial H_c / \partial P)_T$  in the compressibility obtained by differentiation of the molar volume are ignored as negligible, where  $\alpha_{tot}$  is the total volume coefficient of thermal expansion including lattice and electronic terms, and similarly for  $\kappa_{tot}$ .

Taking the first of these expressions, that for the entropy  $S_s(T, P)$ , and dividing through by  $T$  we note the requirement that  $S_s/T \rightarrow 0$  as  $T \rightarrow 0$  due to the opening of a full superconducting gap in the DOS. At the same time if  $\gamma_n$  is constant then  $S_n/T$  is just  $\gamma_n$ . This then imposes a relationship between  $\gamma_n$  and the quadratic term

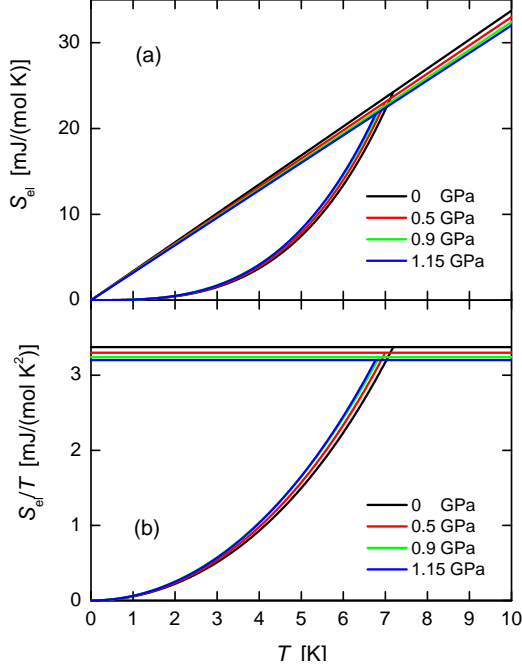


FIG. 4: (Color) The  $T$ -dependence of (a) the electronic entropy in the normal state and superconducting state for pressures of 0, 0.5, 0.9 and 1.15 GPa; and (b) of  $S/T$ .

in  $H_c(T)$ . In particular,

$$\gamma_n = \lim_{T \rightarrow 0} -\mu_o T^{-1} H_c V_M (\partial H_c / \partial T)_P \quad (6)$$

In this way  $\gamma_n$  is calculated from the fits in Fig. 3 and its value is plotted in the inset to Fig. 3. The value at ambient pressure,  $\gamma_n = 3.47$  mJ/(mol K<sup>2</sup>) compares favorably with the value  $\gamma_n = 3.13$  mJ/(mol K<sup>2</sup>) determined from direct specific heat measurements<sup>1</sup>. The pressure dependence of  $\gamma_n$  shown in the inset reveals a dimensionless volume dependence given by  $\partial \ln \gamma_n / \partial \ln V = 3.26 \pm 0.27$  (where we assume a total compressibility of  $\kappa_0 = 0.0205$  GPa<sup>-1</sup>). There have been various estimates of this dimensionless parameter ranging from  $1.7 \pm 0.5$  from thermal expansion measurements<sup>16</sup>,  $1.8 \pm 0.5$  from volume expansion at  $T_c$ <sup>17</sup>, 6.0 based on pressure dependence of  $H_c$ <sup>7</sup> and  $3.1 \pm 0.8$  in good agreement with our present value based on more recent measurements of volume change at  $T_c$  by Ott<sup>18</sup>. Note that this is considerably stronger than the value for the free electron gas  $\partial \ln \gamma_n / \partial \ln V = 2/3$ .

With these relations in place we proceed to calculate the entropy as shown in Fig. 4(a). The linear slope in the normal state is just the above-determined  $\gamma_n(P)$ . The entropy in both states must vanish at  $T = 0$ . A more rigorous test of the polynomial fits to the data is whether  $S_s/T$  also vanishes as  $T \rightarrow 0$  and whether the data preserves monotonic systematics in this region. The  $T$ -dependence of  $S/T$  is plotted in Fig. 4(b) and this indeed shows a quadratic behavior at low  $T$  which is perfectly systematic with increasing pressure and extrapolates to zero as

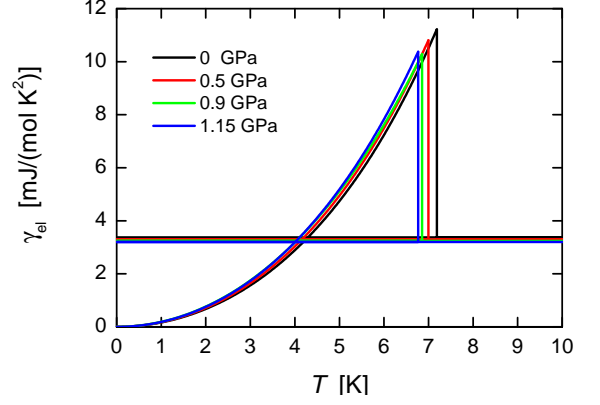


FIG. 5: (Color) The  $T$ -dependence of the specific heat coefficient  $\gamma(T, P)$  in the normal and superconducting states for pressures of 0, 0.5, 0.9 and 1.15 GPa. The small departure from monotonic systematics in the specific heat jump for 0.9 GPa reflects the accumulation of errors in the 2<sup>nd</sup> derivatives.

$T \rightarrow 0$ . In a finite external field the same entropy curves are retraced up to the reduced  $T_c(H)$  value and then the entropy jumps discontinuously to the normal-state value, consistent with a first-order phase transition in magnetic field and second-order when  $H = 0$ .

The condensation energy,  $U_o$  is determined from

$$U_o = \int_0^{T_c} [S_n(T, P) - S_s(T, P)] dT \quad (7)$$

from which we obtain the following values:  $U_o = 47, 43.2, 39.8$  and  $38.6$  mJ/mol for  $P = 0, 0.5, 0.9$  and  $1.15$  GPa, respectively. The condensation energy reduces with pressure due to the twin effects of reduced  $T_c$  and reduced  $\gamma_n$ .

Turning to the specific heat coefficient, this is calculated using the second equation in eqs. (4) and is shown in Fig. 5 for both the normal and superconducting states. The entropy balance is evident from the equal areas above and below the temperature where  $\gamma_s = \gamma_n$ , and is confirmed by the fact shown in Fig. 4(b) that  $S_s/T = \gamma_n$  at  $T_c$ . We find that the jump in  $\gamma(T, P)$  at  $T_c$  is  $\Delta\gamma_c = 7.85, 7.51, 7.05$  and  $7.17$  mJ/(mol K<sup>2</sup>) for  $P = 0, 0.5, 0.9$  and  $1.15$  GPa, respectively. Values of  $\Delta\gamma_c/\gamma_n$  are respectively 2.33, 2.28, 2.18 and 2.24. There is a weak pressure dependence here in this ratio that is not expected with a simple BCS picture where  $\Delta\gamma_c/\gamma_n = 1.55$ . Direct specific heat measurements at ambient pressure have variously obtained  $\Delta\gamma_c = 7.33 \pm 0.3$  mJ/(mol K<sup>2</sup>) (Clement and Quinell<sup>19</sup>),  $7.96 \pm 0.08$  mJ/(mol K<sup>2</sup>) (Shiffman *et al.*<sup>20</sup>) and  $8.13 \pm 0.13$  mJ/(mol K<sup>2</sup>) (Neighbor *et al.*<sup>21</sup>) in good agreement with our ambient result. Combining with the measurement by Horowitz *et al.*<sup>1</sup> of  $\gamma_n = 3.13$  mJ/(mol K<sup>2</sup>) gives  $\Delta\gamma_c/\gamma_n = 2.34, 2.54$  and  $2.60$ , again in good agreement with our present ambient-pressure result. We note that for the purely parabolic form  $H_c = H_c^o \{1 - t^2\}$  then  $\Delta\gamma_c/\gamma_n = 2$  exactly, and so the experimentally observed excess of  $\Delta\gamma_c/\gamma_n$  is a direct indication of the pres-

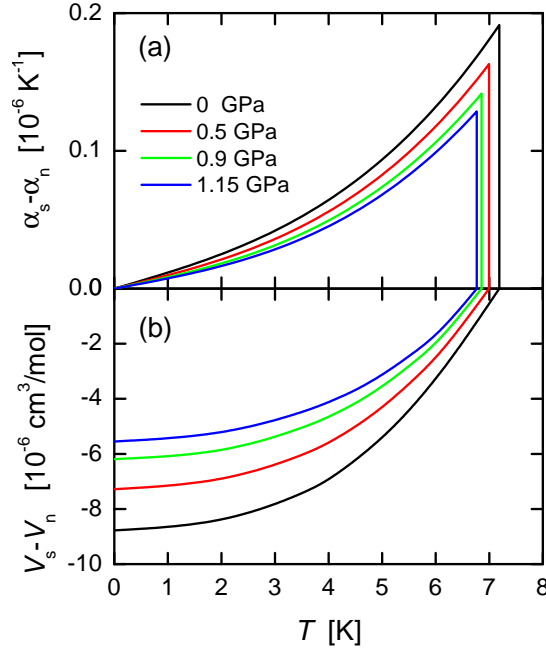


FIG. 6: (Color) (a) The  $T$ -dependence of the difference in volume thermal expansion coefficient between the superconducting and normal states for pressures of 0, 0.5, 0.9 and 1.15 GPa. (b) the difference in molar volume for the same pressures.

ence of a higher order (quartic) term in the  $T$ -dependent critical field.

Finally, Fig. 6(a) shows the calculated difference in volume thermal expansion coefficient between the superconducting and normal states at each pressure and Fig. 6(b) shows the difference in molar volume. Given that the absolute molar volume at  $T = 0$  K is  $18.26 \text{ cm}^3/\text{mol}$  these changes in volume seem extremely small but they are readily measurable. The jumps in thermal expansion coefficient at  $T_c$  in zero field are  $\Delta\alpha = 1.91, 1.63, 1.42$  and  $1.29 \times 10^{-7} \text{ K}^{-1}$  for  $P = 0, 0.5, 0.9$  and  $1.15$  GPa, respectively. We omit the calculations of the electronic compressibility because these involve double derivatives with respect to pressure and here the errors begin to accumulate markedly. Nonetheless the discontinuous jumps in isothermal compressibility may be calculated from the Ehrenfest equation for a second order transition:

$$dT_c/dP = \Delta\kappa/\Delta\alpha \quad (8)$$

Empirically we find that

$$T_c(P) = 7.1863 - 0.3847P + 0.01769P^2 \quad (9)$$

so that the absolute jumps in isothermal compressibility at  $T_c$  in zero field are  $\Delta\kappa = -7.3, -6.0, -5.0$  and  $-4.4 \times 10^{-8} \text{ GPa}^{-1}$  for  $P = 0, 0.5, 0.9$  and  $1.15$  GPa, respectively, while the relative jumps are  $\Delta\kappa/\kappa_0 = -3.56, -2.93, -2.44$  and  $-2.15$  ppm. Direct measurements<sup>22</sup> of the ambient-pressure elastic moduli for Pb in the supercon-

ducting state yield  $\Delta\kappa/\kappa_0 = -4.0$  ppm, again in excellent agreement with our analysis for  $P = 0$  GPa.

We conclude by using the above results to estimate the pressure-dependence of key parameters in the BCS model<sup>23</sup>. The condensation energy is

$$\begin{aligned} \frac{1}{2}\mu_0 H_{c0}(P) &= \frac{1}{2}N(0)N_A\Delta_0^2 \\ &= (47.11 - 7.75P) \text{ mJ/mol} \end{aligned} \quad (10)$$

where  $P$  is in GPa. The jump in specific heat is given by

$$\begin{aligned} \gamma_s - \gamma_n &= 10.2k_B^2 N(0)N_A \\ &= (7.85 - 0.68P) \text{ mJ/(mol K}^2\text{)}. \end{aligned} \quad (11)$$

Therefore, we obtain

$$N(0) = (1.07 - 0.093P) \text{ states/atom/eV} \quad (12)$$

$$\Delta_0 = (11.1 - 0.432P) \text{ K} \quad (13)$$

$$2\Delta_0/k_B T_c = 3.09 + 0.037P. \quad (14)$$

This should be compared with the BCS result  $2\Delta_0/k_B T_c = 3.53$  and the value of  $\Delta_0 = 15.76 \pm 0.05$  K observed from tunneling<sup>24</sup> giving  $2\Delta_0/k_B T_c = 4.37$ .

If, on the other hand, we determine the DOS from the nearly-free electron expression<sup>23</sup>

$$\begin{aligned} \gamma_n &= (2/3)\pi^2 k_B^2 N(0)N_A \\ &= (3.47 - 0.232P) \text{ mJ/(mol K}^2\text{)}. \end{aligned} \quad (15)$$

Then we obtain

$$N(0) = (0.736 - 0.0492P) \text{ states/atom/eV} \quad (16)$$

$$\Delta_0 = (13.7 - 0.653P) \text{ K} \quad (17)$$

$$2\Delta_0/k_B T_c = 3.72 + 0.007P. \quad (18)$$

and the ratio  $2\Delta_0/k_B T_c$  is more or less pressure independent. Finally, using the BCS expression<sup>23</sup> for  $T_c$

$$T_c = 0.85\Theta_D \exp\left(-\frac{1}{N(0)W}\right) \quad (19)$$

where  $\Theta_D$  is the Debye temperature ( $= 96$  K for Pb<sup>23</sup>) and  $W$  is the pairing interaction, then, using eq. (12)

$$W = (0.343 + 0.0167P) \text{ eV} \quad (20)$$

or using eq. (16)

$$W = (0.499 + 0.0143P) \text{ eV}. \quad (21)$$

Here we have used the Gruneisen coefficient  $\gamma_G = -2.6$  for Pb<sup>25</sup>.

In summary, we have measured the pressure dependence of the superconducting critical field in Pb to 1.15 GPa using a clamp cell in a SQUID magnetometer. By using thermodynamic identities we have determined the electronic free energy, entropy, specific heat coefficient,

thermal expansion coefficient and compressibility, including the jumps in these properties at  $T_c$ . The calculated results match rather well the experimentally observed ambient pressure data, where it is available. The present results allow calculation of these parameters as pressure-dependent quantities and an estimation of the

pressure dependence of the density of states, superconducting energy gap and the pairing interaction.

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